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(54) **A method of protecting a surface**

Verfahren zum Schützen einer Oberfläche

Méthode pour protéger un surface

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Description

The invention concerns a method of protecting a surface of a carbonatic material from corrosion, the method comprising treatment of the material surface with an acidic cationic silica sol, the pH of the sol preferably being from about 4 to about 7. The invention also concerns a new silica sol useful for performing the method and a method of preparing the new silica sol. Further, the invention concerns carbonatic material comprising a surface layer of silica, the surface of the silica particles comprising a polyvalent metal oxide/hydroxide.

Many buildings, ordinary houses as well as historical monuments and statues, are made of porous carbonate rich material such as limestone, dolomite, marble or calcareous sandstone which materials are sensitive to pollutants present in the air, particularly the oxides SO_x, NO_x and CO_2 giving acids when dissolved in rain water. It has been established that a major cause of limestone deterioration is acidic rain and dry deposition of SO_2 into the stone pore system, i.e. corrosive reaction progressing between the rainfalls, for which reason also material non-exposed to rain becomes deteriorated.

It has been found that the dominating deterioration factor of carbonatic stone is the formation of a hard black crust on the surface of the stone, the crust mainly consisting of $CaSO_4 \cdot 2H_2O$ (gypsum) and depositions of dust and dirt. The crust detaches very easily from the underlying stone, and when exposed to rain water, the gypsum dissolves and is transported through the pore system deep into the bulk of the stone where it crystallizes during the drying period, disrupting the stone fabric.

A common method of preserving stone involves treatment with water repellents, for example silicon organic products such as alkylsilanes or silicon resins, preventing the penetration of water into the stone and hindering the damage due to crystallization of gypsum in the pores. However, the treatment does not hinder the corrosive reaction at the stone surface and therefore does not counteract the formation of the gypsum crust which can easily be detached from the underlying stone. Further, water solutions of salts appearing behind the silicone treated layers lead to accelerated decay of the stone. Moreover, the silico-organic materials are relatively expensive and must also be applied as solutions in organic solvents.

Another method involves coating of the stone with lime sacrificial layers, introducing fine reactive calcite at the stone surface and thus creating particularly favorable conditions for the corrosive reaction to occur. Therefore, the lime coating treatment must be repeated after a certain time interval, and after some time also the surface of the coated stone can be affected by the corrosive reaction.

US patent 4423096 discloses treatment of ceramic construction materials with a composition comprising a silica sol having finely divided granular ceramic powder suspended therethrough. The patent does not mention cationic sol and treatment of carbonatic material is not mentioned.

US patent 3252917 relates to the production of "salt free" cationic silica sol. The sol is said to be useful for waterproofing building material constructed from hydraulic binding agents such as concrete or mortar, the sol being incorporated together with the other components during preparation of the material. The patent also discloses treatment of asbestos plates, cork plates or the like, but does not mention surface treatment of solid carbonatic material.

US patent 4451338 discloses a method of producing alumina coated silica sols from trivalent aluminum salts.

Thus, there is a current demand for a method of protecting solid carbonatic building material against pollutants present in the air. It is therefore an objective of the invention to provide a method of inhibiting the corrosion caused by acid rain and by dry deposition of SO_2 at the surface of carbonatic materials. It is also an objective of the invention to prevent water from reaching the bulk of a porous material without stopping it from breathing. It is another objective of the invention to provide an effective, non-toxic and comparatively inexpensive agent for treating the surface of a carbonatic material.

According to the invention, the above objectives have been achieved by providing a method of protecting a surface of a carbonatic material, particularly a material having a high content of calcium carbonate and comprising a pore system, the method comprising treatment of the surface with an acidic cationic silica sol, the pH of the sol suitably being from about 4 to about 7, preferably from about 5 to about 7, most preferably from about 5 to about 6. Cationic silica sol refer to an aqueous sol comprising dense, non-agglomerated positively charged particles, the surface of the particles comprising a polyvalent metal oxide/hydroxide, preferably aluminum oxide/hydroxide.

Without being bound to any theory, the following mechanism behind the stone protection is assumed. At slightly acidic pH, i.e. below the iso-electric point of the metal oxide/hydroxide on the SiO_2 particles in the sol, which point in the case of alumina is between 6 and 8, the metal oxide/hydroxide is in its protonated form, the particles thus comprising a great number of positively charged groups. When the surface of a carbonatic material, such as carbonatic stone, is contacted with the weakly acidic sol, the carbonate dissolves slightly and reacts with H^+ to HCO_3^-. The resulting deprotonation of the sol particles brings about a fast increase of the pH in the sol and gelling of the metal oxide/hydroxide near its zero-point of charge. Since the supply of proton-binding species proceeds from the surface of the carbonate grains, the gelling proceeds at the stone surface, coating it with a thin dense protective layer mainly consisting of silica and metal oxide, suitably from about 0.05 to

about 2 mm thick, preferably from about 0.1 to about 0.2 mm thick, partly above the stone surface and partly in the outer pores. The portion above the stone surface should preferably be thinner than 1 mm, most preferably thinner than 0.2 mm. It has been found that the protective layer is effectively prevented from being washed out of the stone surface. The silica protects the carbonatic material against acids and also restrains rain water from penetrating into the stone pore system. On the other hand, the protective layer has been found to be permeable to water vapour, enabling the stone to breath and preventing moisture from being permanently entrapped in the pores.

In order to avoid corrosion caused by easily soluble salts, the silica sol used should contain as small amounts as possible of both dissolved anions and cations. The conductivity at pH 4 should preferably be less than about $3000 \cdot 10^{-6}$ S/cm, most preferably less than about $500 \cdot 10^{-6}$ S/cm. Chloride and other halide ions are particularly harmful, and the content of those ions should preferably be less than 0.05 mol/liter, most preferably less than 0.01 mol/liter.

Cationic silica sols comprising alumina or other polyvalent metal oxides/hydroxides are well known and commercially available, for example under the trademark Bindzil(R) CAT 80 (Eka Nobel AB, Bohus Sweden). The preparation of cationic sols involve surface modification of an anionic sol and is described in numerous patents, for example US patents 3007878, 3252917, 3139406, 3620978, 3719607 3745126 and 3956171, GB patent 1265550 and CA patent 953605. The surface modification does not significally change the size of the silica particles. The average particle size and the particle size distribution can therefor be controlled when preparing the starting anionic silica sol. In order to obtain the required average particle size and particle size distribution, the reaction time has to be carefully controlled at chosen pH and temperature, see for example US patents 2244325 and 2574902. However, most of the commercially available cationic sols are too acidic and contain too much of chloride or other dissolved anions, and must therefore be modified prior to use in the present method. The modification involves purification by removal of chloride and/or other anions, and deacidifying the sol to suitable pH. The purification can be achieved by membrane methods such as dialysis or ultrafiltration, or by ion-exchange.

In a preferred silica sol to be used, the average particle size, i.e. the mean particle diameter by numbers, may for example be within the range from about 1 to about 150 nm, but preferably the average particle size is within the range from about 10 to about 70 nm, and most preferably from about 20 to about 50 nm. The particle size distribution can be from almost monodisperse mean particle size, the standard deviation of the particle diameter for example being less than 10% by numbers of the mean particle diameter, and up to very wide, the standard deviation for example being up to or above about 140% by numbers of the mean particle diameter. Thus, if the mean particle diameter by numbers is about 35 nm, the standard deviation by numbers may for example be from below about 3.5 nm and up to or more than about 50 nm. Suitably, the particle size distribution is wide, the standard deviation of the particle diameter preferably being above about 30%, most preferably above about 55% by numbers of the mean particle diameter, and preferably below about 115%, most preferably below about 85% by numbers of the mean particle diameter. Both relatively large average particle size as well as broad particle size distribution enhance the high density of the silica layer formed at the surface of the treated material.

The molar ratio of metal oxide to silica is preferably within the range from about $2 \cdot 10^{-5} \cdot A$ to about $2 \cdot 10^{-3} \cdot A$, most preferably from about $1 \cdot 10^{-4} \cdot A$ to about $8 \cdot 10^{-4} \cdot A$, A being the specific surface area of the silica particles in m^2 per gram, which area easily can be determined using BET method. If the above ratio is too low the sol becomes unstable, if the ratio is too high the sol becomes more expensive and also unstable. The dry content of the sol is not critical and may for example be from about 5 to about 60% by weight, preferably from about 20 to about 50% by weight. Preferably, the dry content of the sol substantially consists of silica and metal oxide/hydroxide.

The carbonatic material to be protected may for example include carbonatic stone such as limestone, dolomite, marble or calcareous sandstone, but also plaster, lime mortar or concrete. The method is useful for treating plain or painted surfaces of existing buildings, wallings, statues or other monuments, but also for treating blocks of stone or prefabricated building elements made of carbonatic material.

The silica sol may be applied to the surface with conventional coating methods such as brushing, rolling, spraying or dipping, the protective layer being obtained after one or several subsequent treatments. The sol may also be included in a composition containing colorants and/or silicon resins having water repellent properties, thus providing a multi-purpose coating composition.

In a preferred method, the carbonatic material is pretreated with a silica sol capable of penetrating deep into the pore system, preferably more than about 2 mm, most preferably more than about 10 mm. The pretreatment may be performed with an anionic silica sol comprising negatively charged dense non-agglomerated silica particles, the pH of the sol preferably being from about 7 to about 10.

When an anionic silica sol is applied to the surface of a porous material, the sol penetrates into the pores by means of capillary forces. No chemical reaction occurs, but due to decrease of the mean interparticle distance, the sol gels inside the pores. The porous material acts as a sieve which stops larger sol particles at narrowings separating void spaces. When the critical con-

centration of the particles is exceeded, a 3-dimensional gel structure starts to grow and fills the pore space, resulting in a thick layer of silica inside the porous material. The depth of the penetration depends on the silica content in the sol, a low silica content resulting in deep penetration before gelling, in many cases up to 20 or 60 mm. In order to obtain a thick uniform silica layer inside the porous material, the treatment is preferably performed with a diluted silica sol and most preferably repeated one or several times after drying of the first layer. After the final treatment, the surface layer of the carbonatic material is preferably substantially saturated with silica sol.

A deep silica layer gives improved protection of the treated material. Further, the silica gel can transport water and salts dissolved therein out of the pore system, thus avoiding accumulation of the salts in the porous material.

The anionic silica sol should contain as small amounts as possible of metal cations, particularly alkali metal cations such as Na^+, K^+ and Li^+, since these ions may form salts easily soluble in water, involving the risk for the salts to be transported into the pore system inside the treated material where they can crystallize and destroy the material. The content of alkali metals expressed as Na_2O should preferably be less than 0.1% by weight, most preferably less than 0.05% by weight. Therefore, the stabilizing counterions of the sol should mainly consist of other ions, preferably volatile cations such as NH_4^+, evaporating as ammonia from the material treated and leaving a clean alkali metal free protective layer. Further examples of useful stabilizing cations are amines and quaternary amines. The silica content in the sol is preferably from about 5 to about 60% by weight, most preferably from about 10 to about 40% by weight. Regarding the preferred average particle size and particle size distribution, the same values as for the cationic silica sol applies. Suitable anionic sols are commercially available, for example under the trade mark Bindzil$^{(R)}$ 40NH_3/80 (Eka Nobel AB, Bohus, Sweden).

As appears from the above description, a particularly preferred method of protecting a surface of a carbonatic material comprises the following subsequent steps:

(a) treatment with an anionic silica sol resulting in saturation of the material with silica and in formation of a silica layer from just below the surface deep into the pore system of the material treated;

(b) treatment with a cationic silica sol to form a dense protective silica layer at the surface of the treated material.

The invention also concerns a new cationic silica sol and a method of its preparation. The new cationic silica sol comprise dense, non-agglomerated positively charged particles, the surface of the particles comprising a polyvalent metal oxide/hydroxide, preferably aluminum oxide/hydroxide, the pH of the sol being from about 4 to about 7, the standard deviation of the particle diameter being above about 30% by numbers of the mean particle diameter, preferably above about 55% by numbers. Preferably, the standard deviation is below about 140% by numbers of the mean particle diameter, most preferably below about 115% by numbers, particularly below about 85% by numbers. The mean particle diameter by numbers is suitably within the range from about 1 to about 150 nm, preferably from about 10 to about 70 nm, most preferably from about 20 to about 50 nm. Preferably, the content of chloride ions and halide ions is less than about 0.05 mol/liter, most preferably less than 0.01 mol/liter, and the conductivity at pH 4 is preferably less than about $3000 \cdot 10^{-6}$ S/cm, most preferably less than about $500 \cdot 10^{-6}$ S/cm. Additional preferred features of the new sol appear from the described method of protecting a carbonatic material.

The method of preparing the new sol comprise deacidifying and/or removing anions from a cationic sol having suitable average particle size and suitable particle size distribution, the pH of the starting sol however being below about 4, for example from about 2 to about 4, or the conductivity being higher than about $3000 \cdot 10^{-6}$ S/cm, for example from about $3000 \cdot 10^{-6}$ to about $13000 \cdot 10^{-6}$ S/cm, or the content of chloride or halogenide being more than about 0.05 mol/liter. Deacidification and removal of anions may be achieved in the same operation, for example dialysis, ultrafiltration or ion exchange. Suitable starting sols are commercially available, for example the above mentioned Bindzil$^{(R)}$ CAT 80.

The invention further concerns carbonatic building material obtainable by the method of the invention, such as blocks of stone or prefabricated building elements, the material comprising a thin dense surface layer of silica and a polyvalent metal oxide/hydroxide, preferably alumina, the layer being resistent to water but permeable to water vapour, and preferably being from about 0.05 to about 2 mm thick, most preferably from about 0.1 to about 0.2 mm thick. Further, the material preferably comprise a deep layer of gelled silica sol below the surface layer, preferably substantially uniformly distributed within the pores from the surface to a depth of at least about 2 mm, most preferably at least about 10 mm. Such material is obtainable by the present method of protecting a carbonatic material.

The invention is further illustrated through to following examples. The invention is however not limited to these examples, but only to the scope of the appended claims. If not otherwise stated, all percentages and parts refer to % and parts by weight.

EXAMPLE 1: In order to prepare a cationic silica sol according to the invention, the commercially available cationic silica sol Bindzil$^{(R)}$ Cat 80 was modified. The starting sol had a dry content of 43.4% by weight, contained 2.1% by weight of Al_2O_3 and 0.2 mol Cl^- per liter. The pH of the sol was 3.5 and 3.2 ml of 0.1 N NaOH had to be used in order to titrate 1 ml of the sol to pH 7. The

mean particle diameter by numbers was about 35 nm with a standard deviation by numbers of about 25 nm. About 95% by numbers of the particles had a size within the range from about 5 to about 150 nm. 35 ml of the sol were placed in a Servapor(R) dialysis tube and dialyzed into 1.5 liter of distilled water. The dialysis was statical with no water flow or stirring. Every 24 hour the dialyzed sol was transferred into a fresh portion of water. After 120 hours of dialysis, the resulting sol had a dry content of about 30%, pH of 5.45 and contained 0.008 mol Cl^- per liter. Further, only 0.2 ml of 0.1 N NaOH was necessary in order to titrate 1 ml of the sol to pH 7. The dialysis had thus removed chlorides present both as neutral salts and as hydrochloric acid which in the starting sol is present both in free form and as bound to the surface of the sol particles. The resulting modified sol was stable.

EXAMPLE 2: A 5x5x2 cm block was cut from a soft porous limestone from Pinczow - Poland, which is a Miocene sedimentary rock, built of calcitic organic remnants, with porosity of 25% and a bulk specific gravity of 1.75 g/cm^3. One of its surfaces was dipped into cationic silica sol prepared according to example 1 but diluted to a dry content of about 25%. After 20 minutes of impregnation 0.5 g of dry material from the sol, corresponding to 2 g of the sol, had been taken up of the stone which then was allowed to dry in room temperature. SEM (Scanning Electron Microscopy) and XRF (X-Ray Fluorescence) analyses showed that the thickness of the protective layer was about 0.1-0.2 mm. The stone thus impregnated, as well as an untreated stone, were artificially weathered for 96 hours in a stream of humid air (RH 95-100%) having a temperature of 40°C and containing 50 ppm SO_2. SEM and XRF analyses showed that the treated stone contained only trace amounts of the corrosion product $CaSO_4 \cdot 2H_2O$, whereas the untreated stone was considerably corroded.

EXAMPLE 3: In this experiment, an anionic silica sol of the trademark Bindzil(R) $40NH_3/80$ was used, the sol being stabilized with NH_4^+ and containing less than 0.05% of Na_2O, the pH being 9.5. The dry content was 40%, the specific surface area was 80 m^2/g, the mean particle diameter by numbers was about 35 nm with a standard deviation by numbers of 25 nm. About 95% by numbers of the particles had a size within the range from about 5 to about 150 nm. The above sol was diluted to a dry content of about 30%, whereupon a block of lime stone similar to those used in example 2, was impregnated with the diluted sol for 20 minutes. After that time, 2.5 g of the dry material from the sol, corresponding to 8.3 g of the sol, had been taken up by the stone. Then the block was left to dry until constant weight and the impregnation procedure was repeated. After the second impregnation, an excess of silica gel appeared at the stone surface, and further introduction of silica sol into the stone proved impossible. The 2-5 mm deep dense layer of silica significantly reduced the penetration of liquids into the stone, as was established by measuring the capillary suction of water and toluene. However, the silica layer proved permeable to water vapour.

EXAMPLE 4: Blocks of limestone similar to those used in example 2, were first treated with an anionic sol according to example 3 and then treated with a cationic sol according to example 2. After drying, the blocks were artificially weathered in a humid air containing SO_2. Untreated limestone and limestone impregnated just as in example 2 were weathered in the same experiment as reference samples. The artificial weathering involved the following three cycles:

(1) 2 hours treatment in an airstream having a temperature of 40°C, humidity of 95% RH and containing 55 ppm SO_2, the sample being cooled by cold water circulating through the sample holder, resulting in water precipitation on the surface of the sample.
(2) 5 hours treatment in an airstream having a temperature of 40°C, humidity of 95% RH and containing 55 ppm SO_2. The sample is not cooled, resulting in formation of sulfuric acid at the sample surface.
(3) 5 hours treatment in an airstream having a temperature of 40°C, humidity of 40% RH and containing 55 ppm SO_2. The sample is not cooled and the water condensed in the stone evaporates.

The above described cycles were repeated for 96 hours, whereupon the samples were examined by a SEM supplied with an energy-dispersive microanalyser in order to determine the distribution of sulfates, i.e. the corrosion products, in the cross section of the samples. The untreated blocks exhibited a thick corroded layer which showed distinct signs of disintegration. The blocks treated with cationic silica sol only, showed a corroded layer extending to about the same depth but with considerably reduced amount of the corrosion product $CaSO_4 \cdot 2H_2O$ present. The blocks treated with anionic and cationic silica sols and thus comprising a composite silica layer, showed no or very little corrosion products and the state of preservation of their surface could be assessed as perfect.

Claims

1. A method of treating a surface of a carbonatic material, **characterised** in that the method comprises treatment of the material surface with an acidic cationic silica sol.

2. A method as claimed in claim 1, wherein the pH of the sol is from about 4 to about 7.

3. A method as claimed in claim 1 or 2, wherein the silica sol comprises positively charged particles, the surface of the particles comprising aluminum oxide/hydroxide.

4. A method as claimed in any of the claims 1-3, wherein the content of chloride or other halide ions in the sol is less than about 0.05 mol/liter.

5. A method as claimed in any of the claims 1-4, wherein the conductivity of the sol is less than about $3000 \cdot 10^{-6}$ S/cm.

6. A method as claimed in any of the claims 1-5, wherein the mean diameter by numbers of particles in the sol is within the range from about 10 to about 70 nm.

7. A method as claimed in any of the claims 1-6, wherein the standard deviation of the particle diameter of the sol is above about 30% by numbers of the mean particle diameter.

8. A method as claimed in any of the claims 1-7, wherein the method further comprises pretreatment of the carbonatic material with a silica sol capable of penetrating deeper than about 2 mm into the pore system.

9. A method as claimed in claim 8, wherein the pretreatment is performed with an anionic silica sol, the stabilizing counter ions of the sol mainly being volatile cations.

10. A method as claimed in any of the claims 1-9, wherein the carbonatic material is limestone, dolomite, marble, calcareous sandstone, plaster, lime mortar or concrete.

11. Cationic silica sol comprising dense, non-agglomerated positively charged particles, the surface of the particles comprising a polyvalent metal oxide/hydroxide, **characterised** in that the pH of the sol is from about 4 to about 7 and the standard deviation of the particle diameter is above about 30% by numbers of the mean particle diameter.

12. Silica sol as claimed in claim 11, wherein the mean particle diameter is from about 10 to about 70 nm.

13. Silica sol as claimed in any of the claims 11-12, wherein the conductivity is less than about $3000 \cdot 10^{-6}$ S/cm

14. Silica sol as claimed in any of the claims 11-13, wherein the content of chloride and halide ions is less than 0.05 mol/liter.

15. A method of preparing a cationic silica sol according to any of the claims 11-14, the method comprising deacidifying and/or removing anions from a cationic sol having a standard deviation of the particle diameter above about 30% by numbers of the mean particle diameter, the pH of the starting sol being below about 4, or the conductivity being higher than about $3000 \cdot 10^{-6}$ S/cm, or the content of chloride or halogenide being more than about 0.05 mol/liter.

16. Carbonatic building material obtainable by the method according to any one of the claims 1-15, which material comprises a surface layer of silica particles on which a polyvalent metal oxide/hydroxide is bound to the surface.

17. Building material as claimed in claim 16, wherein the material further comprises a layer of gelled silica sol below the surface layer.

Patentansprüche

1. Verfahren zur Behandlung einer Oberfläche von Carbonatmaterial. dadurch gekennzeichnet, daß das Verfahren die Behandlung der Materialoberfläche mit einem sauren, kationischen Siliciumdioxidsol umfaßt.

2. Verfahren nach Anspruch 1, wobei der pH-Wert des Sols etwa 4 bis etwa 7 beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei das Siliciumdioxidsol positiv geladene Teilchen umfaßt und die Oberfläche der Teilchen Aluminiumoxid/-hydroxid umfaßt.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei der Gehalt an Chlorid- und anderen Halogenidionen in dem Sol weniger als etwa 0,05 mol/l beträgt.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Leitfähigkeit des Sols weniger als etwa $3000 \cdot 10^{-6}$ S/cm beträgt.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das Zahlenmittel des Teilchendurchmessers in dem Sol im Bereich von etwa 10 bis etwa 70 nm liegt.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei die Standardabweichung des Teilchendurchmessers des Sols mehr als etwa 30 % des Zahlenmittels des Teilchendurchmessers beträgt.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei das Verfahren ferner die Vorbehandlung des Carbonatmaterials mit einem Siliciumdioxidsol umfaßt, das tiefer als etwa 2 mm in das Porensystem eindringen kann.

9. Verfahren nach Anspruch 8, wobei die Vorbehandlung mit einem anionischen Siliciumdioxidsol erfolgt und die stabilisierenden Gegenionen des Sols

hauptsächlich flüchtige Kationen sind.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei das Carbonatmaterial Kalkstein, Dolomit, Marmor, kalkhaltiger Sandstein, Gips, Kalkmörtel oder Beton ist.

11. Kationisches Siliciumdioxidsol, umfassend dichte, nicht agglomerierte, positiv geladene Teilchen, deren Oberfläche ein Oxid/Hydroxid eines mehrwertigen Metalls umfaßt, dadurch gekennzeichnet, daß der pH-Wert des Sols etwa 4 bis etwa 7 beträgt und die Standardabweichung des Teilchendurchmessers mehr als 30 % des Zahlenmittels des Teilchendurchmessers beträgt.

12. Siliciumdioxidsol nach Anspruch 11, wobei der mittlere Teilchendurchmesser etwa 10 bis etwa 70 nm beträgt.

13. Siliciumdioxidsol nach einem der Ansprüche 11 bis 12, wobei die Leitfähigkeit weniger als etwa $3000 \cdot 10^{-6}$ S/cm beträgt.

14. Siliciumdioxidsol nach einem der Ansprüche 11 bis 13, wobei der Gehalt an Chlorid- und Halogenidionen weniger als 0,05 mol/l beträgt.

15. Verfahren zur Herstellung eines kationischen Siliciumdioxidsols nach einem der Ansprüche 11 bis 14, wobei das Verfahren das Entsäuern und/oder Entfernen von Anionen aus einem kationischen Sol mit einer Standardabweichung des Teilchendurchmessers von mehr als etwa 30 % des Zahlenmittels des Teilchendurchmessers umfaßt, wobei der pH-Wert des Ausgangssols weniger als etwa 4 oder die Leitfähigkeit mehr als etwa $3000 \cdot 10^{-6}$ S/cm oder der Gehalt an Chlorid oder Halogenid mehr als etwa 0,05 mol/l beträgt.

16. Carbonat-Baumaterial. erhältlich nach dem Verfahren nach einem der Ansprüche 1 bis 15, wobei das Material eine Oberflächenschicht von Siliciumdioxidteilchen umfaßt, auf deren Oberfläche ein Oxid/Hydroxid eines mehrwertigen Metalls gebunden ist.

17. Baumaterial nach Anspruch 16, wobei das Material ferner eine Schicht eines gelierten Siliciumdioxidsols unterhalb der Oberflächenschicht umfaßt.

Revendications

1. Procédé de traitement de la surface d'un matériau renfermant des carbonates, caractérisé en ce que le procédé comprend le traitement de la surface du matériau avec un sol acide de silice cationique.

2. Procédé conforme à la revendication 1, dans lequel le pH du sol est compris entre environ 4 et environ 7.

3. Procédé conforme à la revendication 1 ou 2, dans lequel le sol de silice comprend des particules chargées positivement, la surface des particules comprenant de l'hydroxyde/oxyde d'aluminium.

4. Procédé conforme à l'une quelconque des revendications 1 à 3, dans lequel la teneur en ions chlorure ou autres halogénures dans le sol est inférieure à environ 0,05 mole/litre.

5. Procédé conforme à l'une quelconque des revendications 1 à 4, dans lequel la conductivité du sol est inférieure à environ $3000\ 10^{-6}$ S/cm.

6. Procédé conforme à l'une quelconque des revendications 1 à 5, dans lequel le diamètre moyen en nombre des particules dans le sol est compris entre environ 10 et environ 70 nm.

7. Procédé conforme à l'une quelconque des revendications 1 à 6, dans lequel l'écart type du diamètre des particules du sol est supérieur à environ 30 % en nombre par rapport au diamètre moyen des particules.

8. Procédé conforme à l'une quelconque des revendications 1 à 7, dans lequel le procédé comprend en outre le prétraitement du matériau renfermant des carbonates avec un sol de silice capable de pénétrer dans le système des pores à une profondeur supérieure à environ 2 mm.

9. Procédé conforme à la revendication 8, dans lequel le prétraitement est effectué avec un sol de silice anionique, les contre-ions stabilisants du sol étant principalement des cations volatils.

10. Procédé conforme à l'une quelconque des revendications 1 à 9, dans lequel le matériau renfermant des carbonates est du calcaire, de la dolomite, du marbre, du grès calcaire, du plâtre, du mortier ordinaire ou du béton.

11. Sol de silice cationique comprenant des particules denses, non agglomérées chargées positivement, la surface des particules comprenant de l'hydroxyde/oxyde d'un métal polyvalent, caractérisé en ce que le pH du sol est compris entre environ 4 et environ 7 et en ce que l'écart type du diamètre des particules est supérieur à environ 30 % en nombre par rapport au diamètre moyen des particules.

12. Sol de silice conforme à la revendication 11 dans lequel le diamètre moyen des particules est compris entre environ 10 et environ 70 nm.

13. Sol de silice conforme à l'une quelconque des revendications 11 à 12, dans lequel la conductivité est inférieure à environ 3000 10^{-6} S/cm.

14. Sol de silice conforme à l'une quelconque des revendications 11 à 13, dans lequel la teneur en ions chlorure et autres halogénures est inférieure à 0,05 mole/litre.

15. Procédé de préparation d'un sol de silice cationique conforme à l'une quelconque des revendications 11 à 14, le procédé comprenant la désacidification et/ou l'élimination d'anions d'un sol cationique pour lequel l'écart type du diamètre des particules est supérieur à environ 30 % en nombre par rapport au diamètre moyen des particules, le pH du sol de départ étant d'environ 4, ou la conductivité étant supérieure à environ 3000 10^{-6} S/cm, ou la teneur en ions chlorure ou autre halogénures étant supérieure à environ 0,05 mole/litre.

16. Matériau de construction renfermant des carbonates que l'on peut obtenir selon le procédé conforme à l'une quelconque des revendications 1 à 15, lequel matériau comprend une couche de surface constituée de particules de silice à la surface desquelles est lié de l'hydroxyde/oxyde d'un métal polyvalent.

17. Matériau de construction conforme à la revendication 16 dans lequel le matériau comprend en outre une couche de sol de silice gélifiée en dessous de la couche superficielle.